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The Ionic Telomerization of Butadiene¹

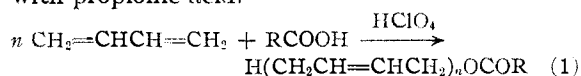
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The perchloric acid-catalyzed telomerization of butadiene with carboxylic acids has been found to yield unsaturated esters containing a plurality of butadiene units in the alcohol portion. The esters containing one, two and three butadiene residues have been isolated, and the molecular weight distribution of the reaction product has been indicated. A mechanism for the acid-catalyzed telomerization of conjugated dienes is proposed.

Previous investigators have synthesized low molecular weight polymers possessing terminal functionality by the polymerization of an unsaturated compound in the presence of a reactant that combines and thus introduces end groups. For example, the free radical-initiated polymerization of styrene in the presence of carbon tetrachloride yields products believed to be terminated by $-\text{Cl}$ and $-\text{CCl}_3$ end groups.² Similarly, the polymerization of ethylene in the presence of hydrogen chloride, chloroform and carbon tetrachloride yields, respectively, *n*-alkyl chlorides,³ α,α,α -trichloroalkanes⁴ and $\alpha,\alpha,\alpha,\omega$ -tetrachloroalkanes.^{4b,5} This type of polymerization has been referred to as *telomerization*, the products as *telomers*, and the agents furnishing the end groups as *telogens*.^{3,4b} It is a type of reaction intermediate between the classical addition reactions of olefins in which one molecule of olefin combines with one molecule of addend and the familiar vinyl polymerizations that give high molecular weight polymers in which the end groups are a minuscule portion of the molecule.

The synthesis of esters of geraniol and related alcohols⁶ from *isoprene* in acetic acid solutions containing sulfuric acid has suggested that telomerization may also occur by an ionic mechanism. Esters of geraniol and related alcohols have also been made from isoprene employing dichloroacetic acid which evidently served as both telogen and catalyst.⁷ However, somewhat different results were obtained by Farmer, who implied⁸ that hydrocarbons were the principal products formed from *butadiene* in a solution of sulfuric acid in acetic acid.

This paper describes the synthesis of a family of esters containing a plurality of butadiene residues in the alcohol portion by the perchloric acid-catalyzed telomerization of butadiene with acetic acid and with propionic acid.



Although sulfuric acid is a sufficiently active cata-

(1) Presented before the Division of Organic Chemistry at the 118th Meeting of the American Chemical Society, Chicago, Illinois, September 5, 1950.

(2) C. C. Price, *Ann. N. Y. Acad. Sci.*, **44**, 366 (1943); J. W. Breitenbach and A. Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

(3) T. A. Ford, W. E. Hanford and J. Harmon, 113th Meeting, American Chemical Society, Chicago, Ill., April, 1948; W. E. Hanford and J. Harmon, U. S. Patent 2,418,832, April 15, 1947.

(4) (a) J. Harmon, T. A. Ford, W. E. Hanford and R. M. Joyce, *This Journal*, **73**, 2213 (1950); (b) W. E. Hanford and R. M. Joyce, U. S. Patent 2,440,800, May 4, 1948.

(5) R. M. Joyce, W. E. Hanford and J. Harmon, *ibid.*, **70**, 2529 (1948).

(6) T. Wagner-Jauregg, *Ann.*, **496**, 52 (1932); T. Lennartz, *Ber.*, **76B**, 831 (1943).

(7) M. Hunt, U. S. Patent 2,460,291, Feb. 1, 1949.

(8) E. H. Farmer and R. C. Pitkethly, *J. Chem. Soc.*, 11 (1938).

lyst⁶ for the telomerization of isoprene, the less reactive butadiene requires a stronger acid, such as perchloric acid.⁹ In the telomerization of isoprene with acetic acid, perchloric acid at 0.1% concentration gave forty-five times as much telomer as did sulfuric acid under the same conditions.

Nature of Products.—Butadiene and acetic acid gave chiefly a mixture of the acetates of alcohols containing a plurality of butadiene residues with one double bond in each residue. Esters containing two butadiene residues formed about 35% of the total product; the fraction containing three residues made up 20%; telomers containing more than three residues furnished another 30%. Approximately 15% of the product was the simple 1:1 adduct of butadiene and acetic acid.

The principal products were esters of linear primary alcohols. However, such esters were not formed exclusively. For example, that portion of the product corresponding approximately to two butadiene residues contained not only the acetate of the linear, primary, doubly-unsaturated alcohol (I), $\text{H}(\text{CH}_2\text{CH}=\text{CHCH}_2)_2\text{OCOCH}_3$, but also four additional components. One was the isomeric ester in which the acetate group was attached in the 3- rather than the 1-position. Another fraction contained an unsaturated hydrocarbon. The other two components were esters. The evidence obtained indicated that one was the ester of a cyclic alcohol; the other probably had a branched-chain structure.

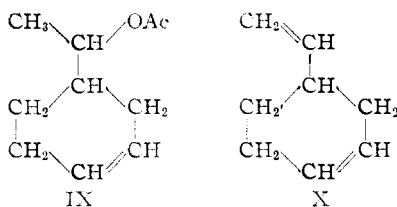
The products obtained when propionic acid was used as telogen were the propionates of unsaturated alcohols containing a plurality of butadiene units. With propionic acid, as with acetic acid, esters of both primary and secondary alcohols resulted. Although the products from propionic acid were less extensively characterized than were those obtained with acetic acid, they appeared to be quite analogous to the latter and differed only in having a higher average molecular weight.

When acetic acid was employed as telogen at 25°, the weight ratio of ester with two monomer units to esters with more than two units was 0.6. With propionic acid at -18° this ratio had the value of 0.2. This indicates either that acetic acid is a more active telogen than propionic acid, or that lowering the temperature favors chain propagation relative to termination.

Evidence of Structure.—In order to establish the course of the reaction, the mixture of products from butadiene and acetic acid at 25° was distilled, and the fraction containing the C₈-acetates (*i.e.*, esters of alcohols containing two butadiene

(9) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York and London, 1940, p. 261.

less double bond than the corresponding acyclic compounds.



Experimental

Materials: Acetic Acid.—Mallinckrodt Chemical Works, Reagent Grade, glacial acetic acid, m.p. 16.00–16.30° was used.

Butadiene.—Phillips Petroleum Company, "Pure Grade" product was distilled directly from the cylinder.

Perchloric Acid.—Mallinckrodt, Analytical Reagent, 70–72% perchloric acid. By titration this material contained 70.70% acid. It had a density of 1.675 g./ml. at 25°. (In the preparation of the catalyst solution, acetic anhydride was added to react with the water present in the aqueous perchloric acid and in the acetic acid.)

Propionic Acid.—The propionic acid used was obtained from the Polychemicals Department of the du Pont Company.

Caution.—Mixtures of perchloric acid with organic materials are known to present serious explosion hazards.¹⁰ In the present work the mixtures were kept out of oxygen balance by limiting the concentration of perchloric acid to 5% or less. Immediately at the end of the reaction, either the perchloric acid was converted to the insoluble potassium salt and removed by filtration or the whole mixture was poured into water and neutralized with aqueous alkali. Although no explosion or other evidence of oxidation by perchloric acid was encountered, it was recognized that there was always the possibility of a violent detonation.

Acetic Acid as Telogen at 25°.—The telomerization was conducted in a 3-l., round-bottomed, one-necked flask equipped with a 2-holed stopper bearing a thermometer and a tube connected to an open-end manometer. The latter served to indicate the pressure and also to act as a safety release in case of excessive pressure. The acetic acid (1718 ml., 1784 g.) and 33.3 ml. of perchloric acid (39.4 g. as HClO₄) were charged into the flask. The vessel was placed in an ice-bath, and 150 ml. (162 g.) of acetic anhydride was added to react with the water present in the reagents. The resulting 2% solution of perchloric acid in acetic acid was cooled until partly frozen and then 500 ml. (343 g.) of butadiene at ca. –70° was added. The stopper was wired in place, the mixture shaken and brought to 25°. The homogeneous reaction mixture exhibited a pressure of about 400 mm. above atmospheric pressure. The reaction was mildly exothermic and the solution turned from colorless to deep amber as the reaction proceeded.

At the conclusion of the 5-hr. reaction period, 200 ml. of a solution of potassium acetate in acetic acid (209 g./l.) was added to neutralize the catalyst. A total of 210 ml. of butadiene was recovered in a Dry Ice trap during the suction filtration of the mixture to remove the potassium perchlorate and during the subsequent distillation of the acetic acid at a pressure of 65 mm.

The crude product was combined with those from five similar experiments and the composite was distilled. Near the beginning of the distillation it was necessary to shut

TABLE I
DISTILLATION OF POLYBUTYLENE ACETATES

	Weight, g.	Boiling point, °C.	Mm.	Total product, %
C ₄ -Acetates	112.0	30–40	7	14.2
C ₈ -Acetates	295.0	38–109	3	37.5
C ₁₂ -Acetates	146.5	108–149	1	18.7
>C ₁₂ -Acetates	235.3			29.6
Total	788.8			

(10) E. Deiss, *Chem.-Ztg.*, **66**, 415 (1942); O. Hackl, *Z. anal. Chem.*, **107**, 385 (1936).

down and filter the mixture to remove potassium acetate which had been precipitated. The several fractions obtained are presented in Table I.

This product was obtained from a total charge of 2058 g. of butadiene, and represents a 38% conversion on a weight basis.

Examination of the C₄-Acetate Fraction.—A corresponding C₄-fraction from a similar experiment was redistilled to obtain a fraction that boiled at 61–64° (67 mm.), *n*_D²⁰ 1.4156. Analysis of this fraction indicated it to be butenyl acetate.

Anal. Calcd. for H(CH₂CH=CHCH₂)OCOCH₃: C, 63.13; H, 8.83; sapon. equiv., 114.1; iodine no., 222. Found: C, 63.31; H, 9.05; sapon. equiv., 114.8; iodine no., 218.

The boiling point of the ester corresponds to that of crotyl acetate.¹¹ There was some lower boiling ester which may have been the isomeric methylvinylcarbinyl acetate.

Examination of the C₈-Acetate Fraction.—A 239-g. portion of the C₈-acetate fraction was fractionally distilled through a Podbielniak Hyper-Cal column (25 mm. diameter) with a 60:1 reflux ratio at a pressure of 4 mm. The boiling points and refractive indices are presented in Fig. 1. Table II lists data for the five apparent components. These components in some cases are a single fraction, in other cases are composites containing up to eighteen fractions.

TABLE II
C₈-ACETATE FRACTIONS COMBINED INTO HOMOGENEOUS GROUPS (SEE FIG. 1)

Component	Fractions	B.p., °C. (4 mm.)	<i>n</i> _D ²⁰	Approx. vol., ml.
I	2–9	63	1.4388	32
II	13	69	1.4550	4
III	15–16	70	1.4474	8
IV	18–22	73–79	1.4520	20
V	25–42	81	1.4492	72

The analyses of selected fractions are presented in Table III.

TABLE III
ANALYSES OF C₈-ACETATE FRACTIONS

	Calcd. for	C, %	H, %	Sapon. equiv.	Iodine number
	H(CH ₂ —CH=CH—CH ₂) ₂ OCOCH ₃	71.39	9.58	168.2	301.8
Found	13	75.51	9.90	220.4	302.7
for	15	72.38	9.64	181.9	303.0
fraction	21	72.91	9.81	179.4	275.1
no.	28	71.84	9.69	164.5	297.8

Component I.—This constituent, which comprises 20% of the C₈-acetate fraction, is believed to be 1,6-octadien-3-yl acetate. The corresponding fraction [b.p. 62° (4 mm.), *n*_D²⁰ 1.4399] obtained from another experiment was analyzed.

Anal. Calcd. for H(C₈H₈)₂OCOCH₃: sapon. equiv., 168.2; iodine no., 301.8. Found: sapon. equiv., 177.7; iodine no., 284.5.

3-Octyl Acetate.—The hydrogenation of 23 g. of the above ester was conducted in acetic acid with Adams platinum catalyst at 30° and 40 lb./sq. in. Distillation of the reduced ester through a 3" helix-packed column gave 15.0 g. of 3-octyl acetate; b.p. 79–82° (13 mm.); *n*_D²⁰ 1.4165 (reported b.p. 90° (10 mm.); *n*_D²⁰ 1.4188 for the optically active ester).¹²

Anal. Calcd. for C₁₀H₂₀O₂: C, 69.72; H, 11.70; sapon. equiv., 172.2. Found: C, 71.07; H, 11.87; sapon. equiv., 181.1.

3-Octanol.—An 11.8-g. portion of the reduced ester was saponified by refluxing it for three hours in a solution of 10 g. of potassium hydroxide and 10 ml. of water in 40 ml. of methanol. The 3-octanol was obtained as a 4.3-g. fraction;

(11) Gredy and Piaux report a boiling point of 128–129° and a refractive index, *n*_D²⁰ 1.4135 for crotyl acetate: B. Gredy and M. L. Piaux, *Bull. soc. chim.*, [5] **1**, 1485 (1934).

(12) Lewis Benzet, *Parfumerie*, **1**, 153 (1943); C. A., **40**, 6758 (1946).

b.p. 75.0° (12 mm.); n_D^{25} 1.4280 (reported b.p. 176–177.5°; n_D^{25} 1.42785 for inactive 3-octanol).¹³

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.93. Found: C, 74.40; H, 13.88.

A sample of the 3-octanol was converted to the acid phthalate ester by treating it with phthalic anhydride according to the procedure of Pickard and Kenyon.¹⁴ The derivative had melting point 59–60°¹⁶ after three recrystallizations from Skellysolve B (*n*-hexane).

Component II.—Figure 1 shows that Fraction 13 possesses a refractive index much above those of neighboring fractions. Its analysis (Table III) gave higher carbon, hydrogen, saponification equivalent and iodine number values than those found for any other fraction. These facts, particularly the high saponification equivalent, indicate that this fraction contains approximately 20% hydrocarbon. The boiling point corresponds to that of a C_{12} -hydrocarbon. This material was not investigated further.

Component III.—The two fractions comprising this group have refractive indices lower than those of adjacent fractions. The analysis of Fraction 15 (Table III) shows that it is an octadienyl acetate with possibly some hydrocarbon contamination. It is suggested that this component may possess a branched carbon skeleton.

Component IV.—This component is apparently a mixture of C_8 -acetates. Its low iodine number suggests that a compound with less than two double bonds per molecule is present. The corresponding fraction from another experiment had an iodine number of 268, which is equivalent to 23% of a mono-unsaturated compound. This may indicate the presence of the isomeric acetate of a cyclic mono-unsaturated alcohol (*e.g.*, α -cyclohexenylethyl acetate).

Component V.—This material represents the principal constituent of the C_8 -acetate mixture and it was examined more fully than were the minor components. Its homogeneity was attested by the constancy of both boiling point and refractive index over the eighteen fractions collected. The analysis of a typical fraction (Fraction 28, Table III) indicates that it is octadienyl acetate.

Octadien-1-ol.—The octadien-1-yl acetate fraction (23 g., b.p. 78° (4 mm.), n_D^{25} 1.4489) from another experiment was saponified in a boiling solution of potassium hydroxide in methanol. The octadien-1-ol was obtained as a 6.7-g. fraction; b.p. 86–88° (10 mm.), n_D^{25} 1.4638.

Anal. Calcd. for $C_8H_{16}O$: C, 76.14; H, 11.18; hydroxyl equiv., 126.2; iodine no., 402.3. Found: C, 75.88; H, 11.23; hydroxyl equiv., 131.4, 128.3; iodine no., 375.1, 380.6.

1-Octyl Acetate.—An octadien-1-yl acetate fraction was hydrogenated at 90° and 1500 lb./sq. in. over a ruthenium catalyst and the product was distilled through a 30" helix-packed column. The 1-octyl acetate so obtained had b.p. 78° (5 mm.), n_D^{25} 1.4188.

1-Octanol.—The 1-octyl acetate (35 g.) prepared above was saponified by heating in a solution of potassium hydroxide in ethanol. The 1-octanol was obtained as a 16.8-g. fraction, b.p. 90° (12 mm.), n_D^{25} 1.4298.

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.93; hydroxyl equiv., 130.2. Found: C, 74.32; H, 13.91; hydroxyl equiv., 135.7.

A portion of the above 1-octanol was converted to the 3,5-dinitrobenzoate, m.p. 61–62° after recrystallization from aqueous ethanol. A mixed melting point with an authentic sample showed no depression.

The *p*-nitrophenylurethan was prepared by adding the 1-octanol to a freshly filtered benzene solution of *p*-nitrophenyl isocyanate. The urethan, after recrystallization from ethanol–water, had m.p. 110–111° and a mixed melting point with an authentic specimen showed no depression.

Examination of the C_{12} -Acetate Fraction.—The C_{12} -acetate fraction from a similar experiment was distilled and representative fractions were analyzed. In order to curtail reactions during the distillation, the material was hydrogenated first. The hydrogenation was carried out in acetic acid solution over a platinum catalyst at 40 lb./sq. in. The reduced esters were distilled at 4 mm. pressure through a

Podbielniak Hyper-Cal column at a 30:1 reflux ratio. The variations in boiling point and refractive index of the 30 fractions obtained indicated the probable presence of four components. The analyses of representative fractions (Table IV) showed that there was a higher proportion of hydrocarbons than was found with the C_8 -acetates.

TABLE IV
ANALYSES OF C_{12} -ACETATE FRACTIONS

	B.p., °C. (4 mm.)	n_D^{25}	C, %	H, %	Sapn. equiv
Calcd. for $H(CH_2)_{12}OCOCH_3$			73.63	12.36	228.4
Found for fraction no.					
4	107	1.4545	74.54	11.30	250.5
7	110	1.4392	75.11	12.13	263.5
19	119	1.4618	77.97	12.01	518.2
30	140	1.4658	73.06	10.71	212.4

Fractions 4 and 7 are principally the telomeric esters containing three butadiene units. Fraction 19, however, appears to be approximately one-half hydrocarbon. The boiling point of this fraction corresponds to that of a butadiene tetramer. Fraction 30 has a low saponification equivalent and a high boiling point. This may be due to the presence of glycol diacetates.

Comparison of Perchloric and Sulfuric Acids as Catalysts.—Perchloric and sulfuric acids were compared as catalysts for the telomerization of isoprene at 25°. The catalysts were used as 0.1% solutions in acetic acid. A control experiment was conducted in which no catalyst was added to the acetic acid.

In each experiment the isoprene (145 ml., 100 g.) was added to 300 g. of an acetic acid solution of the catalyst. The mixture was maintained at 25° for four hours, then poured onto ice and the acetic acid was neutralized with sodium hydroxide. The product, along with remaining isoprene, was extracted with ether, and the extract was dried over calcium chloride. The ether and isoprene were then distilled through a short column, and the residue was weighed.

The experiment in which the catalyst was perchloric acid yielded 94.6 g. of product. Analysis of this material showed that it averaged approximately twelve isoprene residues per ester group.

Anal. Calcd. for $H(CH_2\overset{CH_3}{\underset{|}{C}}=CHCH_2)_{12}OCOCH_3$: C, 84.86; H, 11.48; sapn. equiv., 877.4. Found: C, 84.44; H, 11.48; sapn. equiv., 865.

The experiment in which sulfuric acid was employed yielded 2.0 g. of product which had the fruity odor characteristic of esters. From the experiment in which no catalyst was used 0.5 g. of residue was obtained. It did not possess the fruity odor characteristic of the telomeric esters. Perchloric acid is accordingly a much more powerful catalyst than sulfuric acid, and gave forty-five times as much product as did sulfuric acid under the same conditions.

Propionic Acid as Telogen at –18°. Preliminary Experiments.—A similar procedure to that already described for acetic acid was employed in experiments with propionic acid as telogen. Preliminary tests were conducted at temperatures of 0° and below in order to ascertain requirements for operability.

It was found that certain combinations of propionic acid, perchloric acid and butadiene formed two liquid layers when cooled. In order to prevent this from occurring during the telomerization experiments, a series of tests was conducted to define the limits of miscibility. Mixtures of the three components were prepared, and the temperature above which a single phase existed was determined (Fig. 2).

Telomerizations were conducted on a small scale at temperatures of 0 and –18°. At 0°, reaction times of four hours and 22 hours, respectively, gave conversions to telomer of 35 and 105% (wt. of telomer/wt. of butadiene). At –18°, a conversion of 27% was obtained in 26 hours. In the above experiments, the concentration of perchloric acid in the propionic acid was 5% in contrast to the 2% concentration employed with acetic acid at 25°.

Telomerization of Butadiene with Propionic Acid at –18°.—A 5% solution of perchloric acid in propionic acid was prepared by dissolving 130 ml. of 70% aqueous perchloric

(13) Schimmel and Co., Semi Ann. Rept., April, 1913 (*Chem. Zentr.*, **84**, I, 1973 (1913)).

(14) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **103**, 1944 (1913).

(15) Pickard and Kenyon (ref. 14), reported melting point 62–63° for 3-octyl hydrogen phthalate.

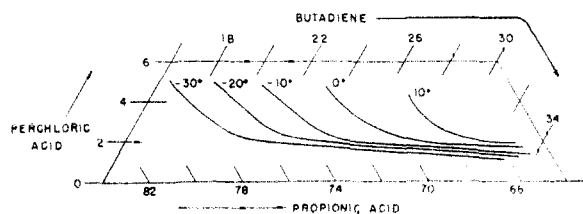


Fig. 2.—Phase diagram for the ternary system propionic acid-butadiene-perchloric acid; compositions are expressed in weight per cent. and temperatures in °C.

acid and 500 ml. of propionic anhydride in 2380 ml. of propionic acid. This solution was cooled in a Dry Ice-bath to -18° , and 600 ml. (410 g.) of butadiene was added. The concentration of butadiene in this reaction mixture was only half that used in the preliminary tests referred to above. The resulting clear solution was placed in a refrigeration unit where the temperature was maintained at -18° for 70 hours. The reaction mixture turned from a light yellow to a clear, deep amber.

At the end of the reaction period, 880 ml. of a solution of potassium acetate in glacial acetic acid (180 g./l.) was added. The mixture was poured onto ice and the propionic acid was neutralized by the slow addition of concentrated aqueous sodium hydroxide. The product was then extracted with ether. The ether extract was dried over calcium chloride and, after removing the ether, the product was distilled through a 10" Vigreux column (Table V). The conversion to telomer was 25% on a weight basis.

TABLE V
DISTILLATION OF POLYBUTENYLENE PROPIONATES

Fraction	Boiling point °C.	Mm.	Weight, g.
1	28	2	21.5
2	30-60	2	15.3
3	70-165	1	33.1
4	150-178	0.6	7.9
Residue			24.4

The C_3 -propionate fractions (2 and 3) from the above distillation were combined with those from two similar experiments, and the composite was distilled at 4 mm. through a Podbielniak Hyper-Cal column (13 mm. diameter). From the distillation twenty-four fractions of approximately 3 ml. each were obtained (Fig. 3).

The distillation curves for the first eleven fractions are very similar to the curves for the C_3 -acetates (Fig. 1). From this analogy it is proposed that Fractions 2 to 4 are octadien-3-yl propionate, and that Fractions 8 to 11 are octadien-1-yl propionate. The analyses of Fractions 3 and 9 (selected as typical) indicate that they are octadienyl propionates.

Anal. Calcd. for $H(C_4H_8)_2OCOC_2H_5$: C, 72.49; H, 9.95; sapon. equiv., 182.3; iodine no., 278.6. Found for Fraction 3: C, 72.76; H, 10.18; sapon. equiv., 190.4; iodine no., 261.4. Found for Fraction 9: C, 72.05; H, 9.99; sapon. equiv., 183.9; iodine no., 266.1.

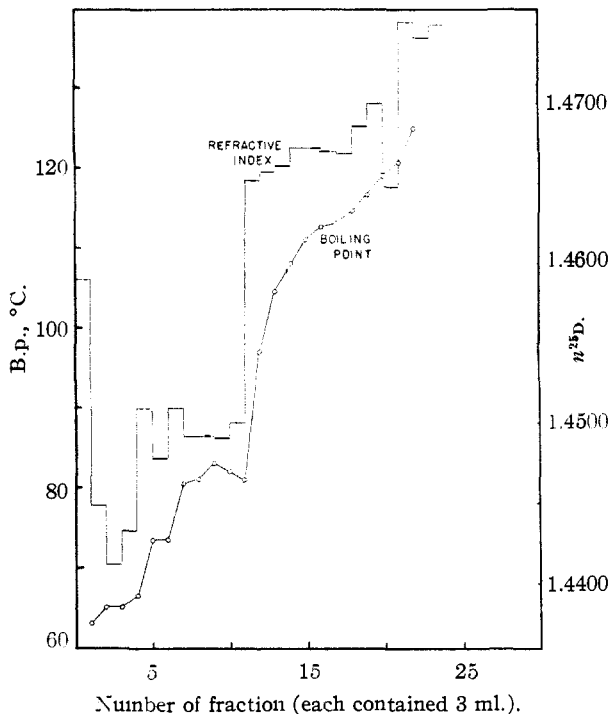


Fig. 3.—Distillation of butadiene-propionic acid telomers. Distillation conducted through a Podbielniak Hyper-Cal column (13 mm. diameter) at 4 mm. pressure with a 30:1 reflux ratio. The charge consisted of 138 g. of telomer, 1 g. of hydroquinone, and 1 g. of potassium acetate.

The C_3 -propionate fraction comprised 12% of the total product, whereas the higher propionates totaled 66%. The ratio of C_3 -propionate to higher propionates was therefore 0.2. This is a marked contrast to the results obtained with acetic acid at 25° in which the corresponding ratio was 0.6.

Examination of the C_{12} -Propionate Fraction.—The distillation of the crude C_3 -propionate fraction showed that it included an appreciable quantity of the C_{12} -propionates (*cf.* Fig. 3). Analysis of Fraction 16 indicates that it is a triply unsaturated C_{12} -propionate with possibly some hydrocarbon contamination.

Anal. Calcd. for $H(C_4H_8)_3OCOC_2H_5$: C, 76.22; H, 10.24; sapon. equiv., 236.3; iodine no., 322.2. Found for Fraction 16: C, 77.25; H, 10.43; sapon. equiv., 257.5; iodine no., 266.9.

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